Influence of Magnetic Fields on Performance of Organic Solar Cells

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on Performance of Organic Solar Cells

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Solar energy is one of the most important renewable source of energy conversion into electricity. Different technologies have been developed to improve the photovoltaic solar cells efficiency. Among these cells, polymer solar cells have received extensive attention due to their advantageous characteristics such as light weight, mechanical flexibility, inexpensive, and large area processability. This article highlights the fundamental energy conversion processes in excitonic solar cells, and introduces a general background on the influence of magnetic fields on performance of polymer-inorganic hybrid cells. Finally, in order to fashion devices and to advance the power conversion efficiency of organic solar cells, a proposal is presented which rely on the employment of an external magnetic field.

1. Introduction

Since electricity is ubiquitously used to power many different means of our modern life that do work for humans, solar energy in the form of light is one of the most prominent renewable sources of energy that can be converted to the more practical form of electricity. Solar energy is a promising energy source that can help mitigate global climate change, reducing greenhouse gas emissions and protect the environment. In fact, there exist many potential renewable energy technologies in which their strategy is based on the harnessing of solar energy such as photovoltaic (PV) cells that their systems could directly produce electricity from sun-light; photoelectrochemical (PEC) cells wherein electrochemical decomposition reactions are driven directly by light; and solar-thermal systems which they could employed either to heat working fluids or to help drive desired chemical reactions. There have been extensive efforts invested in the development of this field with the objective of maximizing efficiency and output power from solar cells at device-level and solar farms at system-level. Different types of solar cells have been developed and widely used for photovoltaic devices ranging from conventional solar cells – which most of them are fabricated

from silicon - to excitonic solar cells[1,2] – in which small molecules, polymers, or quantum dots are used as light absorbing materials. Polymer solar cells (PSCs) or organic solar cells (OSC) have received extensive attention owing to their advantageous characteristics such as their light weight, inexpensive, mechanical flexibility, and large area processability.[3] The goal of this article is to shed light on two issues: (i) to highlight fundamental energy conversion processes in excitonic solar cells, in particular polymer-inorganic hybrid cells, and (ii) a brief insight into the influence of magnetic fields on performance of these solar cells. Finally, in order to fashion devices and to advance the power conversion efficiency of organic solar cells, a proposal is presented which rely on the employment of an external magnetic field.

2. Excitonic Solar Cells

2.1. Photovoltaic Materials

Organic materials include conjugated polymers and small molecules exhibit p-type or n-type semi-conducting properties owing to their conjugated configuration that allows direct electronic transitions of their π- electrons across the band gap of minimal energy difference. These conjugated molecules have high absorption coefficients above 10^5 cm^{-1}.[4] Owing to this property, polymer solar cells can be much thinner (hundreds of nanometers), than many of their inorganic counterparts. The exciton diffusion length in polymers is short, typically less than 10 nm[5] and up to a micrometer in high-quality small molecule films, which is considered as a critical dimension for photovoltaic devices. The hole mobility in most polymeric devices is 10^{-1} - 10^{-7} cm^2 V^{-1} s^{-1}.[6]

2.2. Photovoltaic Processes

Photovoltaic processes comprise three consecutive steps: i) absorption of incident lights leading to the formation of excited states bounded electron-hole pairs (excitons); ii) excitons diffusion to an interface leading to charge separation; and iii) transport of the separated electrons and holes to the cathode and anode, respectively. Electronic excitations in excitonic solar cells produce Coulombically bound electron-hole pairs called excitons, and hence cannot generate a photocurrent. In photovoltaic device, electron donor/acceptor heterojunctions are employed to generate charge carriers, at which excitons must diffuse to the junction without recombining as a result to the energy offset in the lowest unoccupied molecular orbital (LUMO) between donor and acceptor materials.[7-9] For example, excitons in silicon have a binding energy of 20 meV, whereas thermal energy at room temperature (kT) is ~ 25 meV. Hence, illumination of silicon generates free carriers in the bulk, which segregate to the electrodes due to the build-in potential of the p-n junction. In sharp contrast to inorganic solar cells, their organic dyes and polymers counterparts suffer from great localization of photoexcited states owing to their weak intermolecular interactions and low dielectric constants (ε_r = ~ 3-4).[4-10] With exciton binding energies greatly exceeding kT, illumination of excitonic solar cells generates tightly bound electron-hole pairs. In order to separate charge, the exciton must diffuse to the junction before deactivating to the ground state. Since the lifetime of the exciton in organic dyes and conjugated polymer films is very short (~ 1 ns), the exciton diffusion lengths (L_D), [$L_D = (D\tau)^{1/2}$ - where D = diffusion coefficient; τ = the exciton lifetime], are much shorter (~10 nm) than the optical absorption pass

length (~ 100-200 nm). Therefore, a limited part of excitons can diffuse to the junction as in the case of planar heterojunction solar cells. Exciton dissociation takes place as long as the band offset energy at the junction is greater than the exciton binding energy in the material from which it was generated. The exciton splitting in organic photovoltaics can easily achieved when the domain size of donor and acceptor materials is smaller than the diffusion length.[11,12]

3. Polymer-Inorganic Hybrid Cells

Most polymers are soluble in organic solvents and their optical and electrical properties can easily be tuned. Owing to their good mechanical properties, they can be cast onto any substrate in a variety of ways, including manufacturing-friendly roll-to-roll processes. Most hybrid devices comprise an interpenetrated network of blended electron donor and acceptor materials, known as a bulk heterojunction (BHJ), where the band offset at the extended interface induces dissociation of photo-generated excitons (Figure 1). These cells are suffered from inefficient charge transport due to the discontinuous percolation pathways.

The external quantum efficiency of photovoltaic devices (η_{EQE}) is determined by the product of the photon absorption efficiency (η_A), the exciton dissociation (η_{ED}), and the carriers collected by the electrodes of the device (η_{CC}), [$\eta_{EQE} = \eta_A \, \eta_{ED} \, \eta_{CC}$]. The polymer photovoltaic devices suffer from the poor exciton and charge transport. In order to maximize the efficiency of these devices, some approaches suggest to use nanowire array anodes as an ideal structure,[6,13] or employing an orthogonalized geometry to normalize the junction to the substrate.[13]
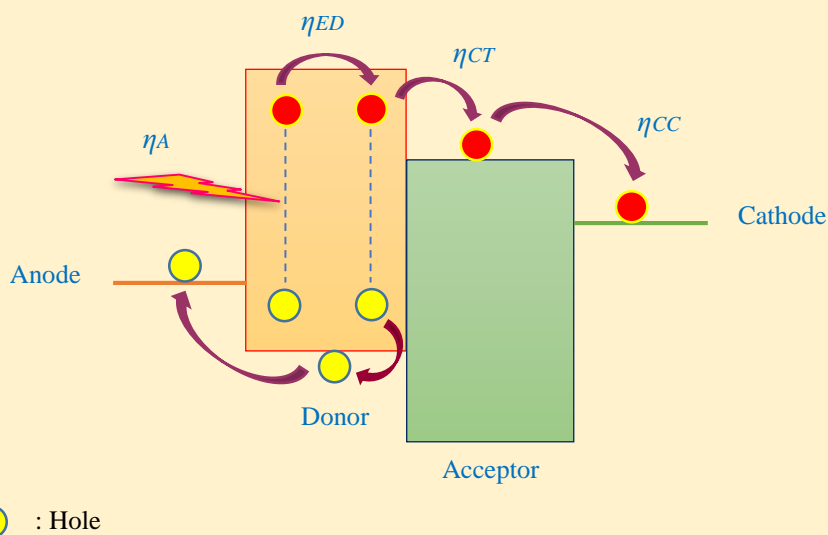

Figure 1. Schematic illustration of band gap arrangement in a bulk heterojunction solar cell.

In bulk heterojunction with inorganic-polymer hybrid cells, the inorganic electron-transporting materials have been fabricated from nanoparticle networks, which serve as the electron conduction medium. While the nanoparticle of narrower band gap materials, such as PbS[14], and PbSe[15] act as a complementary absorber

and an electron transporter. In these devices, exciton dissociation is significantly slower than in the fastest polymer bulk heterojunctions,[16] and is limited by the potential barrier at the interface,[17] as well as the non-ideal density-of-states overlap between the polymer and inorganic phase. In addition, electron transport and recombination rates are very sensitive to the nanoparticle morphology. However, polymer hybrid PVs are considered as the least expensive and easily manufactured classes of nanoparticles solar cells.

The energetic and geometric parameters affecting the exciton dissociation efficiency (η_{ED}) are vital to the performance of hybrid cells. For instance, exciton splitting at the ZnO/P3HT interface is both thermodynamically and kinetically favored[18] (Figure 2). However, the interface charge separation between P3HT and ZnO is poor. It was shown that the addition of polycrystalline TiO_2 shell (~5 nm) improved the efficiency of these devices.[19] Polymer confinement can lead to conformational changes that are detrimental to exciton diffusion and hole transport.
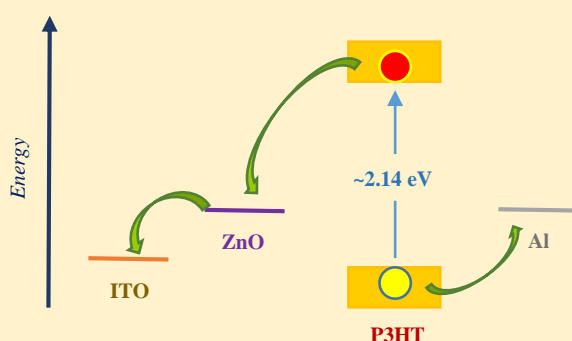

Figure 2. Schematic illustration of band diagram for ZnO nanowire-P3HT polymer solar cell. Excitons are generated in the P3HT and split at the nanowire surface. P3HT = poly(3-hexylthiophene).

4. Magnetic Field Effect

External magnetic field can impact the photocurrent in organic semiconductors, although they are intrinsically nonmagnetic materials. Such a phenomenon is related to the interaction of external magnetic field and internal magnetic field associated with the paramagnetic excited states in these materials, such as triplet excitons (s=1) and free electrons and holes (s=0.5). This interaction leads to change of singlet/triplet ratio of polaron pairs, which, hence, leads to the change of photocurrent. Therefore, the photocurrent of these materials can be modulated by the external magnetic field.[20] In fact, the utilization of external magnetic field can improve the power conversion efficiency of photovoltaic devices, as a result of the dissociation, interactions, and recombination processes of excited states in polymer solar cells.

The singlet exciton generated by light absorption can be partially converted into triplet excitons, owing to hyperfine interaction (HFI) and spin-orbit coupling (SOC), leading to both singlet and triplet excited

states in organic molecules.[21] The triplet excitons exhibit high binding energy and long life time as compared to singlet excitons,[22] which can impact the PV process in polymer solar cells.

It was demonstrated that under the influence of magnetic field, the higher PV efficiency corresponds to a more efficient exciton dissociation (η_{ED}) into free charge carriers in cells containing phosphorescent heavy-metal complexes, such as Ir(ppy)$_3$ **1**, Ir(mppy)$_3$ **3**, and PtBPQ **4** (Figure 3), wherein the light absorption-generated excited states are mainly triplet excitons, while singlet excitons are dominant excited states in cells containing the fluorescent dye molecules, such as Alq$_3$ **2** (Figure 3).[23] In fact, the diffusion length in the phosphorescent dyes is longer than that of the fluorescent dyes.
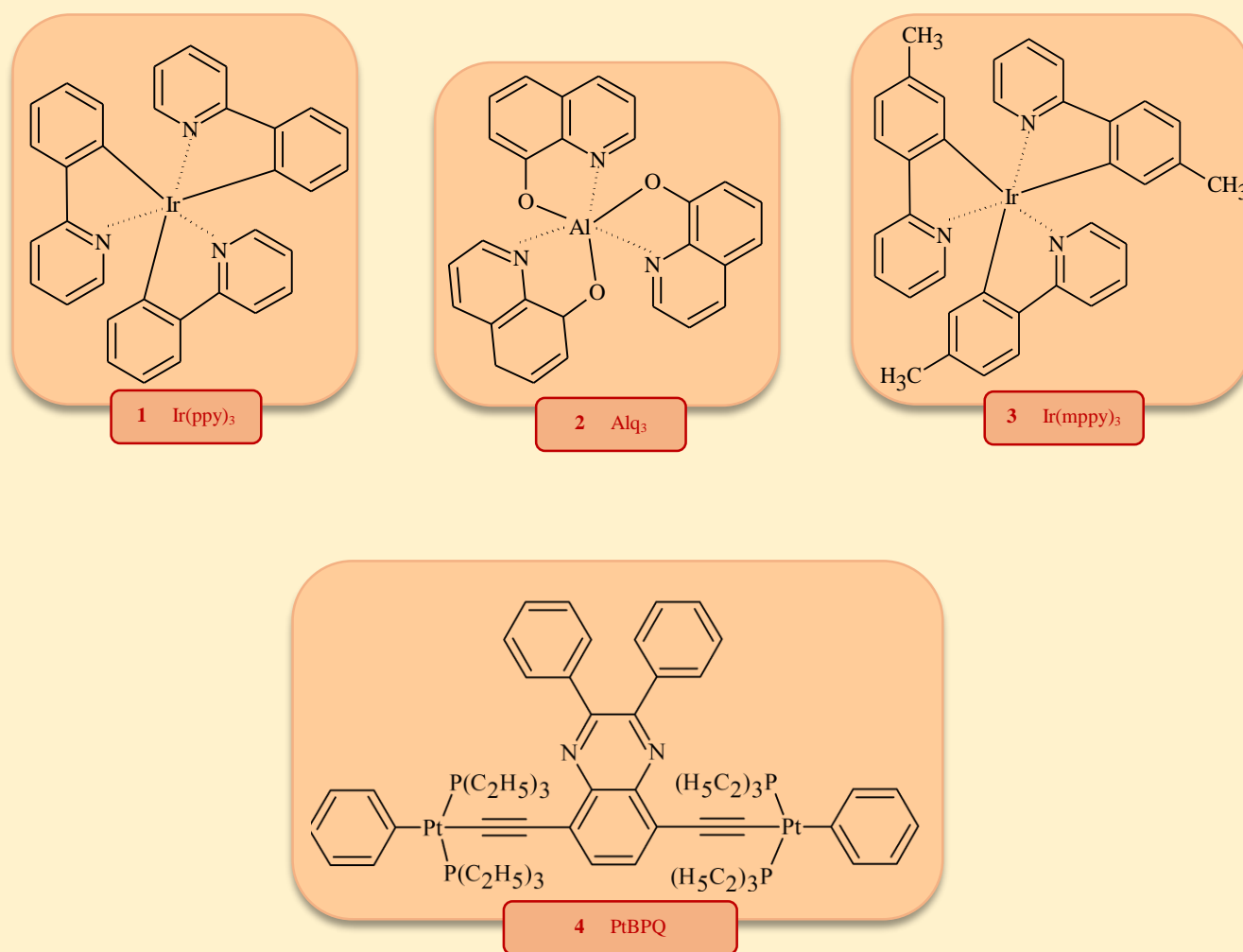

Figure 3. The chemical structures of fluorescent dye molecules and coordination phosphorescent complexes.

Due to different binding energies, lifetimes, and diffusion lengths, the singlet and triplet excitons can have different contributions to the generation of photocurrent. The host-guest system is usually used as the emitting layer of the phosphorescent light-emitting device. Host materials are fluorescent small molecules or polymers and guest materials are doped phosphorescent molecules covalently linked to the host materials. A certain energy match should exist between the host and guest. Therefore, electro-luminescent phosphore-scence emission could be achieved through energy transfer from the host to the guest. The polymer materials incorporating aromatic molecules have weak SOC and thus limited triplet states under photo-excitation. The coordination complexes of Ru, Re, Os, Ir, Pt are widely used in the field of electrolumine-scent phosphors, which have a high quantum efficiency and a short triplet state lifetime such as PtBPQ **4** (Figure 3).

5. Proposed Approach

Magnetite nanoparticles (NPs) have been incorporated in a wide range of applications in magneto-optics. For example, Fe_3O_4 NPs have been employed in tunable filters[24] and optical switches[25] that operate under magnetic fields owing to the magneto-optical properties of Fe_3O_4 NPs. In fact, magnetite is a narrow-gap semiconductor. Magnetite NPs exhibit a wide nonlinear absorption band of visible radiation, and are able to change their electric polarizability when exposed to low-intensity visible radiation. Such change in polarizability is induced by the intraband phototransition of NPs and charge carriers.

In order to fashion devices and to advance the power conversion efficiency of polymer solar cells, a proposal is presented, as a hypothetical strategy, which it relies on a vertical array of bulk-heterostructures PV cells operated under the influence of magnetic field.

The proposed construction of p-type-intrinsic-n-type (p-i-n) coaxial solar cells is shown in Figure 5. The proposed bulk-heterojunction films comprise strong-SOC complexes, iridium(III)pentmethylcyclo-pentadienyl complexes $(Ir(C_p^*ClL))$ **1** (Figure 4), doped a conjugated polymer poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) **2** (Figure 4) as weak-SOC matrix polymers in the presence of [6,6]-phenyl-C_{61}- butyric acid methyl (PCBM) **3** (Figure 4) as a strong electron acceptor. A thin film of this active material is sandwiched between an aluminum-doped zinc oxide nanowires (ZnO:Al) and a flexible transparent indium tin oxide (ITO) coated on plastic polyethylene terephthalate (PET). The proposed $[Ir(C_p^*ClL):MEH-PVV:PCBM]$ solar cell may realize PV efficiency in bulk-heterojunction devices through the optimization of exciton dissociation, exciton-charge reaction, and reduction of charge recombination.

The proposed polymer solar cell can then be fabricated by depositing the ZnO:Al onto the thin film of bulk-heterojunctions coated on the flexible transparent ITO substrate. As a speculation, Neodymium magnet can be used as a source of magnetic field. In view of advanced developments in bulk-heteruojunction polymer solar cells, a wide range of manipulations can be introduced into this model solar cell.
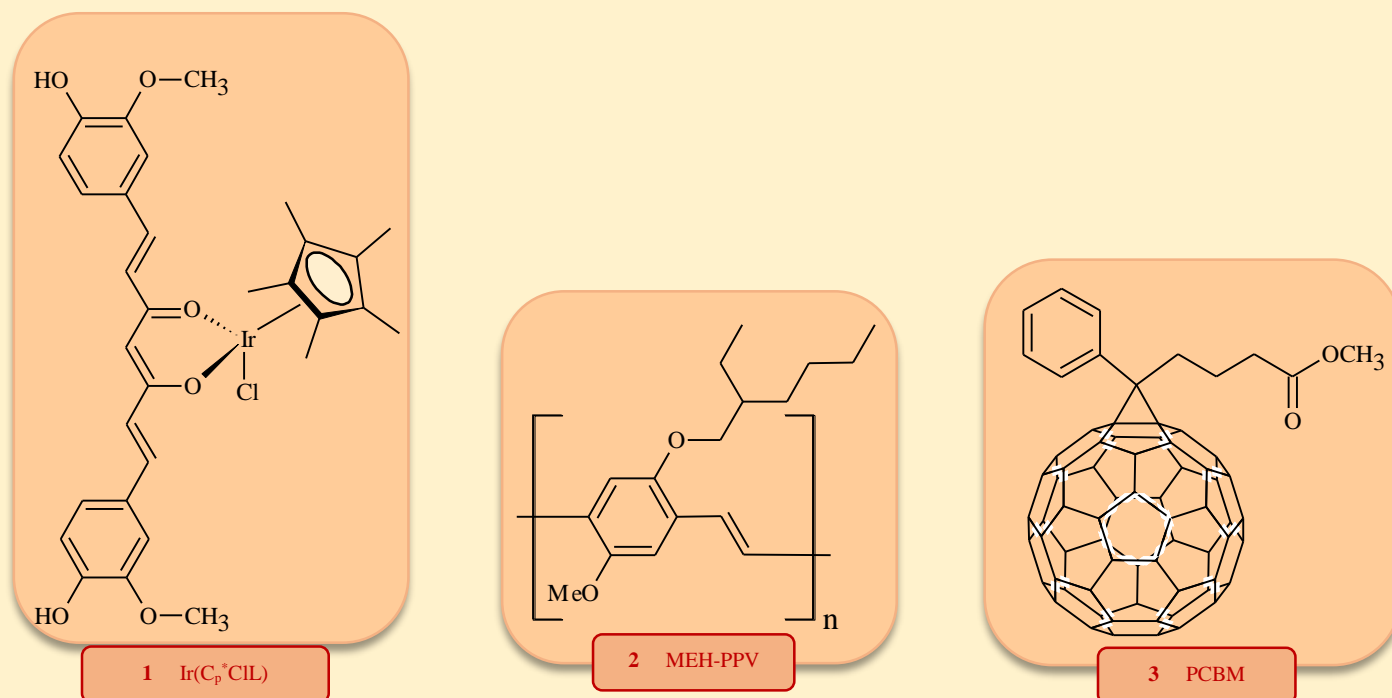
Figure 4. The chemical structures of Ir(C_p^*ClL) complexes [L: ligand], MEH-PPV, and PCBM molecules.
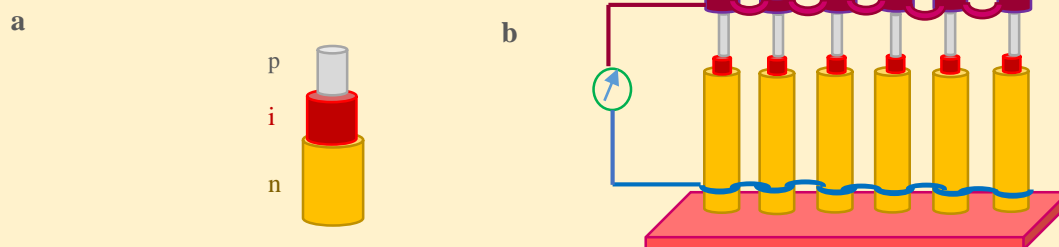

Figure 5. a) Schematic illustration of a single array of p-i-n solar cell. b) Schematic illustration of coaxial PV solar cell with metal contacts deposited on the p-core and n-shell.

The expected scenario is that the triplet exciton ratio would be increased upon the dispersion of Ir(C_p^*ClL) due to the enhancement of spin-orbit coupling. Furthermore, the dispersed iridium complex would reduce the recombination of dissociated charge carriers through changing the singlet and triplet

ratios. Introducing of PCBM into MEH-PPB may dissociate all the excitons and polaron pairs in the polymer matrix. Based on the modification of spin-orbit coupling, it is expected that adjusting exciton dissociation, exciton-charge reaction, and recombination of dissociated charge carriers may form a new route to improve the performance of polymer bulk-heterojunction solar cells.

6. Conclusion

The article highlights the fundamental energy conversion processes in bulk-heterojunction solar cells, and introduces a general background on the influence of magnetic fields on the performance of polymer-inorganic hybrid solar cells. In addition, a proposed model of an archetypal bulk-heterojunction photovoltaic solar cell is introduced, which may result in a dramatic performance increase, while exhibiting good device stability.

References

1) D. Cahen, G. Hodes, M. Gratzel, J. F. Guillemoles, I. Riess, *J. Phys. Chem. B,* **2000***, 104,* 2053-2059.
2) B. A. Gregg, *J. Phys. Chem. B,* **2003***, 107,* 4688-4698.
3) V. Shrotriya, *Nature Photonics,* **2009**, *3,* 447–449.
4) S. E. Gledhill, B. Scott, B. A. Gregg, *J. Mater. Res.,* **2005***, 20,* 3167-3179.
5) P. Peumans, V. Yakimov, S. R. Forrest, J. *Appl. Phys.,* **2003**, *93,* 3693.
6) K. M. Coakley, M. D. McGehee, *Chem. Mater.,* **2004***, 16,* 4533-4542.
7) C. Deibel, V. Dyakonov, *Rep. Prog. Phys.*, **2010**, *73*, 096401.
8) H. Ohkita, S. Ito*, Polymer,* **2011**, *52*, 4397−4417.
9) F. Gao, O. Inganäs, *Phys. Chem. Chem. Phys.,* **2014**, *16*, 20291−20304.
10) L. Dou, J. You, Z. Hong, Z. Xu, G. Li, R. A. Street, Y. Yang, *Adv. Mater.,* **2013**, *25*, 6642−6671.
11) G. Yu, J. Gao, H. C. Hummelen, F. Wudl, A. J. Heeger, *Science,* **1995**, *270*, 1789−1791.
12) J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B. Holmes, *Nature*, **1995**, *376*, 498−500.
13) B. Kannan, K. Castelino, M. Majumdar, *Nano. Lett.,* **2003***, 3,* 1729-1733.
14) S. A. McDoland, G. Konstantatos, S. G. Zhang, P. W. Cyr, E. J. D. Klem, L. Levina, E. H. Sargent, *Nat. Mater,* **2005**, *4,* 138-142.
15) D. H. Cui, J. Xu, T. Zhu, G. Paradee, S. Ashok, M. Gerhold, *Appl. Phys. Lett.,* **2006**, *88,* 183111-183111-3.
16) Y. Kanai, J. C. Grossman, *Nano Lett.,* **2007**, *7,*1967-1972.
17) C. Anghel, V. Derycke, A. Filoramo, S. Lenfant, B. Giffard, D. Vuillaume, J. P. Bourgoin, *Nano Lett.,* **2008**, *8,* 3619-3625.
18) J. E. Kroeze, T. J. Savenije, M. J. W. Vermeulen, J. M. Warman, *J. Phys. Chem. B,* **2003**, *107*, 7696-7705.
19) L. E. Greene, M. Law, B. D. Yuhas, P. D. Yang, *J. Phys. Chem. C,* **2007**, *111,* 18451-18456.
20) F. Ito, T. Ikoma, K. Akiyama, A. Watanabe, S. T. Kubota, *J. Phys. Chem. B,* **2005***, 109*, 8707-8717.
21) C. Daniel, D. G.uillaumont, C. Ribbing, B. Minaev, *J. Phys. Chem.,* **1999**, *103*, 5766.
22) F. Q. Guo, Y. G. Kim, J. R. Reynolds, K. S. Schanze, *Chem. Communi.,* **2006***, 17,* 1887-1889.
23) H. D. Burrows, M. Fernandes, J. S. Melo, A. P. Monkman, S. Navaratnam, *J. Am. Chem. Soc.*, **2003**, *125*, 15310-15311.
24) T. Liu, X. Chen, Z. Di, J. Zhang, *Appl Phys Lett,* **2007**, *91,*121116.
25) S. H. Xia, J. Wang, Z. X. Lu, F. Zhang, *Int J Nanoscience,* **2011**, *10*, 515–520.

Snapshots of some topics of interest of recent notable advances in chemistry

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One-pot Procedure for Synthesis of Stannylbiaryls

A convenient one-pot procedure is highlighted for sequential fluorostannylation-arylstannylation of arynes to construct stannylbiaryls of structural diversity.

Taking advantage of the good chemoselectivity and functional group-compatibility of the moderate polarization in the carbon-tin bonds, this makes organostannanes as highly reactive platform in bond-forming reactions.

In this context, the team of Yoshida described a convenient one-pot procedure for the synthesis of biarylstannanes through sequential fluorostannylation-arylstannylation of arynes. Sequential fluoro-stannylation of 3-methoxybenzyne **2** in 1,2-diethoxyethane (DEE) at 0 °C in the presence of tributyltin fluoride **1**, KF, and 18-crown-6, followed by the addition of 3-methoxybenzyne **2** and copper(I) 2-thiophene-carboxylate (CuTC) at 130 °C provided a regioisomeric mixture of stannylbiaryls **4** in 56% yield (82:18) and the unreacted product from the first step 2-fluoro-6-methoxyphenylstannane **3** (17% yield) (Scheme).
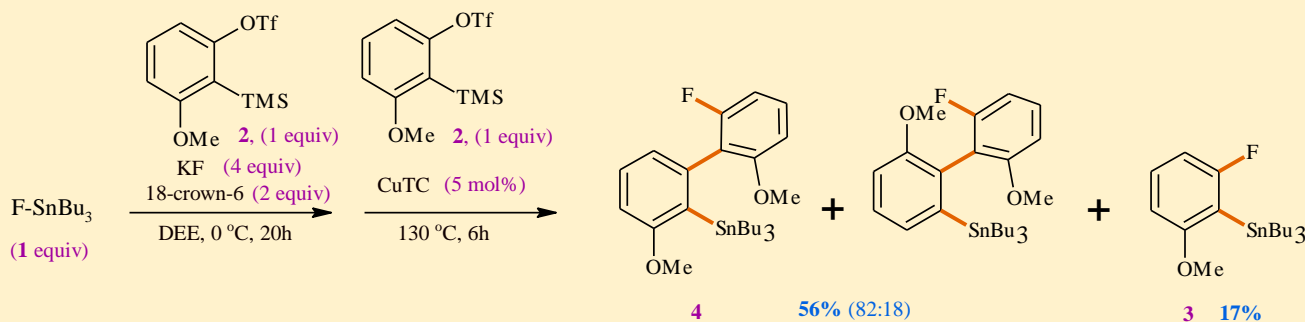
Scheme 1. Preparation of biarylstannanes.

A variety of difficult to synthesize stannylbiaryls by conventional procedures, can be accomplished via this pathway.

Review

H. Tanaka, I. Osaka, H. Yoshida, *Chem. Lett.,* **2019**, *48,* 1032-1034.

Synthesis of Sterically Hindered Quaternary Carbons via Cu-catalyzed Radical and Cation Crossover Reaction System

Radical and cation crossover reaction system was employed for three component coupling of alkenes, alcohols, and α-bromocarbonyl compounds (as a tertiary alkyl source) in the presence of copper catalyst at room temperature to generate complex quaternary carbons possessing an ether moiety.

Generation of a quaternary carbon possessing various functional groups is a challenging procedure, whereas the current methodologies suffer from many drawbacks due to the highly congested structure of quaternary carbons.

Nishikate reported an efficiently Cu-catalyzed radical-cation crossover reaction system, in which a three-component, alkenes **1**, α-bromocarbonyl esters **2**, and alcohols **3** were reacted in the presence of copper catalyst, PMDETA (multidentate ligands), $EtN(i\text{-}Pr)_2$ (base), $Zn(OTf)_2$ (additive), and (CH_2Cl_2) (solvent) at room temperature to afford a complex quaternary carbon possessing various functional groups including nitro, allylic, alkyne, unsaturated ester, amino, or alkyl halogen groups in moderate to good yield (Scheme 1).
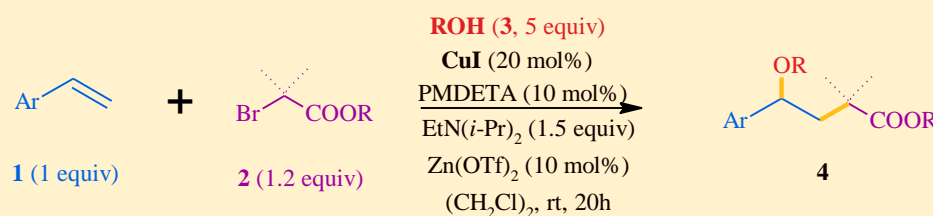
Scheme 1. Synthesis of complex aliphatic chains possessing functionalized quaternary carbons via radical and cation crossover reaction systems.

An example for effective synthesis of a cyclic compounds is shown in Scheme 2. Mechanistic studies revealed that the reaction involves both radical and cationic species.
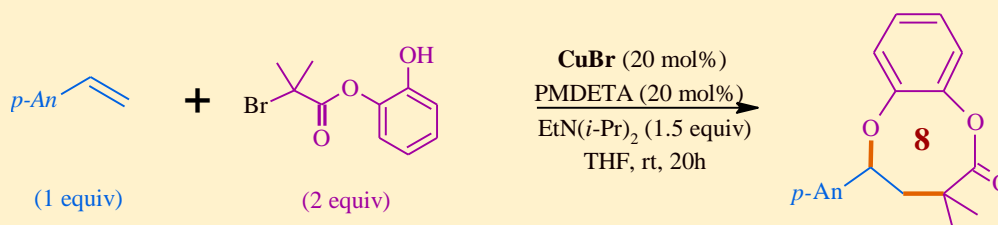
Scheme 2. Cyclization reaction.

This reaction successfully demonstrated the control of two active species, the radical and the cation.

Review

T. Nishikata, *Bull. Chem. Soc. Jpn.,* **2019**, *92*, 1419-1429.